Low Temperature Specific Heat of Amorphous (Co_<1-x>Mn_x)_<100-y>B_y Alloys

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Synopsis

The low temperature specific heat (C_p) for the $(Co_{1-x}Mn_x)_{100-y}B_y$ amorphous alloy series has been studied in the temperature range between 0.4 and 50K using a pumped ^{3}He-cryostat. Below about 10K, C_p for all the present samples can be well fitted to the ordinary expression $C_p = \gamma T + \beta T^3$. The linearly temperature-dependent coefficient γ depends strongly on Mn concentration, that is, with increasing Mn concentration, γ values remarkably increase, for example γ of $Co_{76}B_{24}$ is 5.9mJmol^{-1}K^{-2}, while that of $(Co_{0.6}Mn_{0.4})_{76}B_{24}$ is 15.6mJmol^{-1}K^{-2}. This rather large γ value cannot be explained only by the electronic term and must be attributed to the large magnetic contribution presumably due to the frustration in the spin system. The large γ values also have been obtained in the other amorphous spin glass alloys such as Fe-Ni-P-B, Fe-Zr and Co-Y. On the other hand, Mn concentration dependence of Debye temperature has a discontinuity at certain Mn concentration which corresponds to the same Co/Mn ratio at which the martensitic phase change occurs in the crystalline Co-Mn alloy. This discontinuity reflects a change in phonon behavior which must arise from substantial differences in the amorphous microstructure.

I. Introduction

Co-Mn-B amorphous alloys are one of the interesting object in studying the magnetic and electric properties because these alloy series contain both the ferromagnetic and antiferromagnetic interactions, where the competition of both interactions may yield the frustration in the spin system which results in the spin glass feature

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in certain region of alloys. The magnetic measurements such as magnetization and low field susceptibility have revealed that the magnetic phase diagram of this alloy exhibits ferromagnetic phase (F), reentrant spin glass one (RSG) and pure spin glass one (PSG) dependent on both Mn and B concentrations[1].

Usually spin glass alloys have a large linear magnetic contribution to the specific heat, for example amorphous Fe-Zr[2,3] has a large γ value ($\gamma > 20 mJmol^{-1}K^{-2}$), where γ is a linear coefficient of the specific heat. This large value cannot be explained only by the electronic specific heat and therefore its origin must be attributed to the magnetic contribution. In our present alloy series we also obtained rather large γ values of about $15 mJmol^{-1}K^{-2}$ in the spin glass region.

As another interesting feature in our alloys, we observed a sharp discontinuity in the concentration dependence of the Debye temperature. This must be related to the amorphous microstructure.

In the previous paper we have briefly reported the results of the low temperature specific heat and the ac susceptibility measurements in $(Co_{1-x}Mn_x)_{76}B_{24}$ amorphous alloys[4]. In this report, in order to make clear more precisely and systematically the electronic feature in our spin-glass alloys we present the Mn and B concentration dependence of the specific heat at low temperatures in the amorphous series $(Co_{1-x}Mn_x)_{100-y}B_y$ ($0 \leq x \leq 0.5$, $11 \leq y \leq 33$). For simplicity we refer to this alloy series as CMBX-Y (where X=100x, Y=y), henceforth.

II. Experimental

The amorphous samples used in this study were produced by a melt quenching method from mother alloys. All the samples thus obtained were confirmed to be in the amorphous single phase by an X-ray Debye Scherrer method.

The specific heat measurements were made using a standard heat-pulse technique in a pumped ^{3}He cryostat. The samples with a mass of approximately 0.5 to 1g were mounted onto a copper addenda, which held both Ge and C resistance thermometers and a wire-wound heater. Measurements were performed from about 0.4 to 50K using a standard heat-pulse technique in which energy was added to the combined addenda-sample system by means of a heater and the resulting temperature change was determined from a Ge or C resistance thermometer. The thermal capacity of the addenda was measured in a separate experiment. The thermometers were calibrated against four-lead standard Ge-thermometers above 1.5K and against ^{3}He vapor pressure below 2K.

III. Results and Discussion

Figure 1 shows the typical examples of the specific heat data plotted as log C_p vs. log T for CMB20-24 (Fig.1a) and CMB40-24 (Fig.1b) samples. Both curves exhibit monotonic increases with increasing temperature. The low temperature specific heat C_p in magnetic metals and alloys can generally be described by the following equation,

$$C_p = C_E + C_L + C_M + \cdots\cdots . \qquad (1)$$

The first term represents the electronic specific heat, which is related to the density of state at the Fermi level $N(\varepsilon_F)$ through the relation,

$$C_E = \gamma T = (1/3)\pi^2 k_B^2 N_\gamma(\varepsilon_F)T, \qquad (2)$$

where k_B is the Boltzmann constant and $N_\gamma(\varepsilon_F)$ the enhanced electron density of state, which is related to the bare density of state $N_0(\varepsilon_F)$ as $N_\gamma(\varepsilon_F)=(1+\lambda)N_0(\varepsilon_F)$, where λ is the electron-phonon enhancement factor. The second term in Eq.(1) is related to the lattice specific heat and ordinarily obeys the T^3 law at low temperatures ($T \lesssim 10K$) as

$$C_L = \beta T^3 = (12/5)\pi^4 R(T/\Theta_D(0))^3, \qquad (3)$$

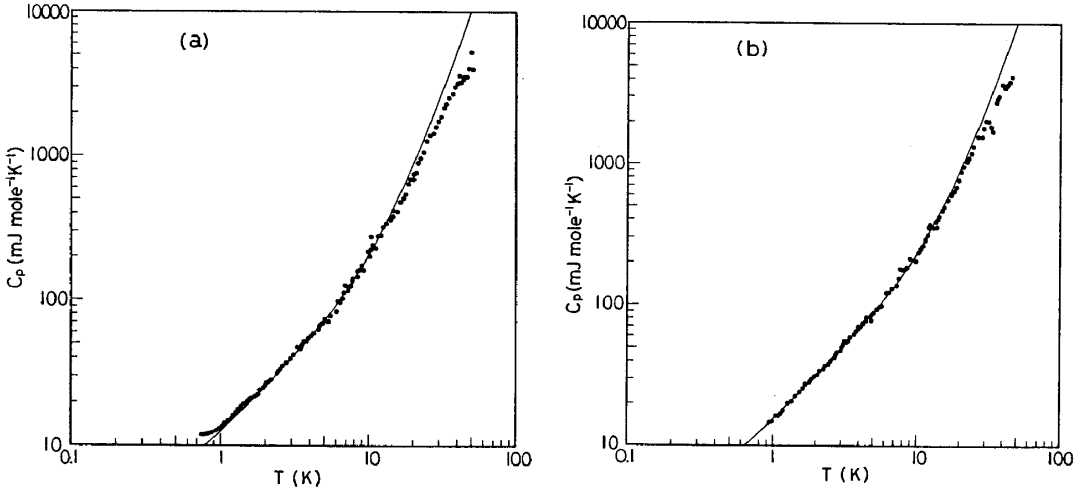

Fig. 1 Temperature dependence of the specific heat plotted as log C_p vs. log T for (a)$(Co_{0.8}Mn_{0.2})_{76}B_{24}$ and (b)$(Co_{0.6}Mn_{0.4})_{76}B_{24}$. Solid curves present the results of the calculation using $C_p = \gamma T+\beta T^3$.

where R is the gas constant and $\Theta_D(0)$ the low temperature limit of the Debye temperature. At higher temperatures, where the T^3 law is not valid, the lattice heat capacity is often expressed by the effective Debye temperature, $\Theta_D(T)$, which is determined by fitting the full Debye model to the heat-capacity data. The third term in Eq. (1) represents the magnetic contribution upon specific heat, which is usually expressed as $\sigma T^{3/2}$ in the case of ferromagnetic material, where the coefficient σ is determined by the spin wave stiffness coefficient D as $\sigma = 0.113 k_B (k_B/D)^{3/2}$ [5]. While in the case of spin glass materials a large linear contribution ($\propto T$) can be expected. Thus in the present alloy the experimentally derived linear coefficient γ, now including the magnetic contribution, is expressed as,

$$\gamma = \gamma_{\text{electronic}} + \gamma_{\text{spin glass}} + \gamma_{\text{non-cryst}}. \qquad (4)$$

Consequently the third term in Eq.(1) in the present alloy is expressed as $C_M = \gamma_{\text{spin glass}} T$. The third term in Eq.(4) means the two-level configurational tunneling effect associated with a disordered lattice[6] and is usually very small.

The specific heat in the present alloys is satisfactorily fitted to the ordinary equation below about $T \sim 10K$:

$$C_p = \gamma T + \beta(0) T^3 \qquad (5)$$

At higher temperature region, Eq.(5) is no longer valid because the other terms of phonon contribution, for example δT^5 term, can not be ignored and also the magnetic contribution due to the spin-glass ordering becomes complex, meaning that the higher order contribution, such as $\beta_{\text{spin-glass}} T^3$, would not be ignored. In Fig. 2 the specific heat data of CMBX-24 (Fig. 2a), CMB20-Y (Fig. 2b) and CMB40-Y (Fig. 2c) are exhibited in the ordinary form of C_p/T against T^2. These data are slightly more scattered due to small masses of specimens. As shown in these figures, all the data points in each sample lie roughly on a straight line between $T^2 = 5K^2$ and about $120K^2$, suggesting the validity of Eq.(5). The specific heat C_p calculated from Eq.(5) using γ and $\beta(0)$ values derived from the C_p/T-T^2 fitting is also expressed in Fig. 1 by solid curves.

As already mentioned above, the magnetic contribution due to the spin wave $\sigma T^{3/2}$ must exist in the ferromagnetic region, and usually this causes a downturn tendency in the C_p/T-T^2 curve at the lower temperature region. But the present results do not show any apparent downturn in the curves. The reason may be ascribed to a large D value

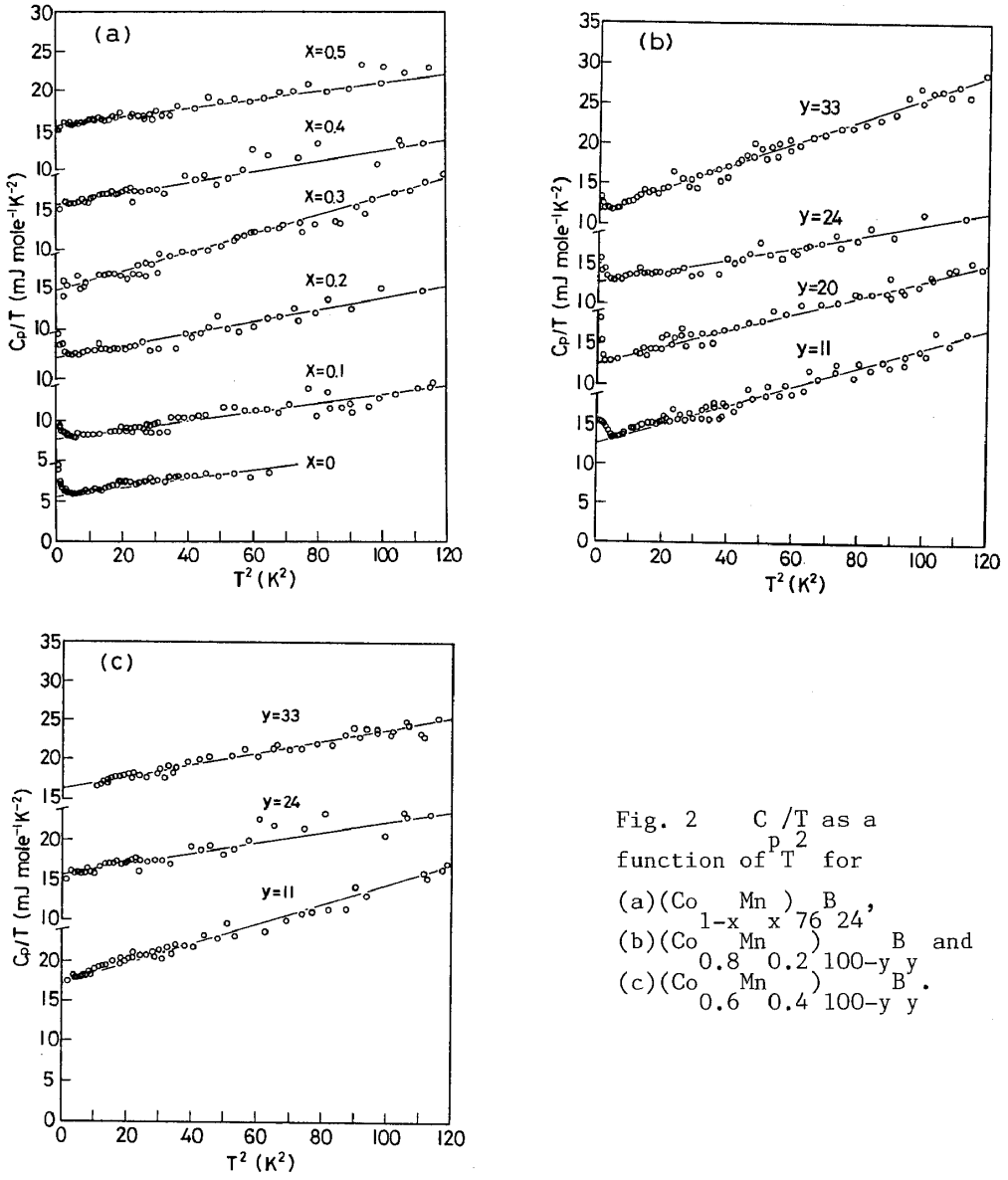

Fig. 2 C_p/T as a function of T^2 for (a)$(Co_{1-x}Mn_x)_{76}B_{24}$, (b)$(Co_{0.8}Mn_{0.2})_{100-y}B_y$ and (c)$(Co_{0.6}Mn_{0.4})_{100-y}B_y$.

in the present alloys. On the other hand, in Fig. 2a and 2b the Co-rich samples (CMBX-24 (X=0, 10 and 20) and CMB20-Y) exhibit a slight upturn in C_p/T vs. T^2 curves at the lowest temperature region. This reason is not clear yet. One possible origin is ascribed to a nuclear spin contribution from the ^{59}Co nuclei at very low temperatures. Mizutani et al. observed[7,8] the upturn in the C_p/T-T^2 curve at low temperature region in the amorphous Co-Fe (or Ni)-Si-B and Co-Y alloys and they discussed this upturn based on the contribution of Co-nuclear specific heat having a form of $C_N = \sigma_n T^{-2}$, where σ_n is the nuclear specific heat coefficient. In the present stage it is difficult to elucidate the origin of this upturn definitely. As mentioned above,

from these figures we can thus determine the linear coefficient γ and the low temperature limit of Debye temperature $\Theta_D(0)$ by using Eqs.(5) and (3). All the values of γ and $\Theta_D(0)$ are compiled in Table 1. As shown in this Table, γ values in CMB40-Y are rather larger than those in CMB20-Y.

Figure 3 shows the Mn concentration dependence of γ values of CMBX-24 series. As shown in this figure, γ increases remarkably between x=0.1 and 0.3 and keeps almost constant above x=0.4. It has been clear from the magnetic measurement[1] that samples of x=0 and 0.1 are ferromagnetic and those of x=0.2 and 0.3 are in reentrant spin glass and those of x=0.4 and 0.5 are in pure spin glass. The magnetic contribution to the linear term in low temperature specific heat is quite small in the ferromagnetic alloys, permitting an accurate determination of the $\gamma_{electronic}$ value within the error of less than 5% below about 4K. However the spin glass alloys, for example Fe-Ni-P-B[9] and Fe-Zr[2,3], have a large linear term in specific heat. So it is very difficult to separate the electronic contribution from the magnetic one. In the present alloy series the electronic term may be less that 10mJmol^{-1}K^{-2}. So excess amount in γ must be caused by the large spin glass contribution. The origin of the large linear term in

Table 1 Several parameters derived from the specific heat C_p.

$(Co_{1-x}Mn_x)_{100-y}B_y$		γ	β	$\Theta_D(0)$	magnetic phase
x	y	(mJmol^{-1}K^{-2})	(mJmol^{-1}K^{-4})	(K)	
0.2	11	12.6	0.120	253	F
0.4	11	17.0	0.115	256	RSG
0.2	20	12.4	0.106	264	F
0.0	24	5.9	0.048	346	F
0.1	24	7.8	0.056	326	F
0.2	24	12.5	0.077	293	RSG
0.3	24	14.9	0.080	253	RSG
0.4	24	15.6	0.069	304	PSG
0.5	24	15.5	0.053	321	PSG
0.2	33	11.7	0.140	240	RSG
0.4	33	16.4	0.076	295	PSG

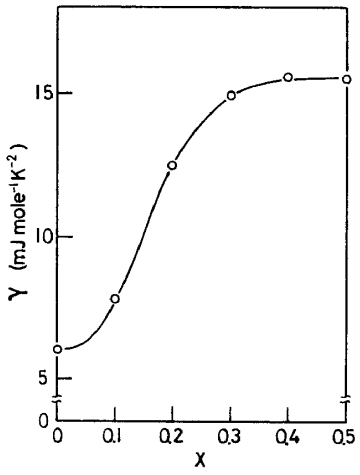

Fig. 3 Mn concentration dependence of γ for $(Co_{1-x}Mn_x)_{76}B_{24}$.

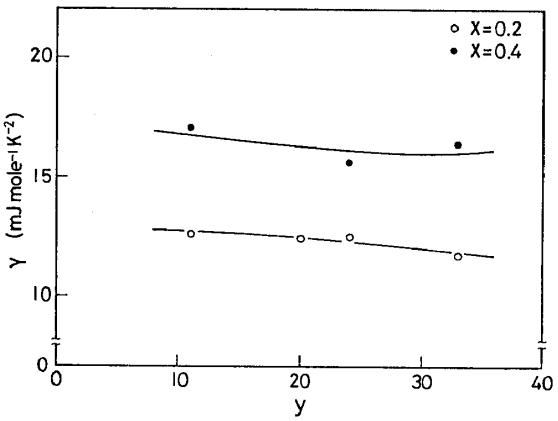

Fig. 4 B concentration dependence of γ for $(Co_{1-x}Mn_x)_{100-y}B_y$ for x=0.2 and 0.4.

spin glass alloys has been investigated by several authors. Soukoulis and Levin[10,11] investigated the magnetic specific heat of the cluster spin glass and deduced that the magnetic specific heat per cluster at low temperature is described by $C_M = C_M^{inter} + C_M^{intra}$, where C_M^{inter} arising from intercluster interaction is linear in temperature as in the Edward-Anderson model[12]. Marshall[13] also obtained an αT-type magnetic specific heat by assuming localized spins to be in a near-zero magnetic field, where α is the linear coefficient in dilute spin glass alloys. Moreover, Mizutani and Takeuchi[7] recently calculated the magnetic specific heat C_m in terms of a computer-simulated amorphous spin-glass model and deduced that at low temperature region C_m in a spin glass state is approximately linear in temperature.

As shown in Fig. 4 the γ values are clearly different between CMB20-Y and CMB40-Y alloys, namely γ values of CMB40-Y are larger than those of CMB20-Y by about 4mJmol^{-1}K^{-2}. It is rather strange that γ values do not change so much with increasing B content for both the series. In other words, γ values seem to be strongly dependent on the Co/Mn ratio rather than on their state (F, RSG and PSG). For example, CMB20-11 is ferromagnetic and CMB20-33 is in RSG, but both γ values are nearly same. Therefore it must be noted that the contribution of the magnetic specific heat to the linear term depends essentially on the content of Mn atoms which may cause the frustration in the spin system. That is, even though the effect of the frustration

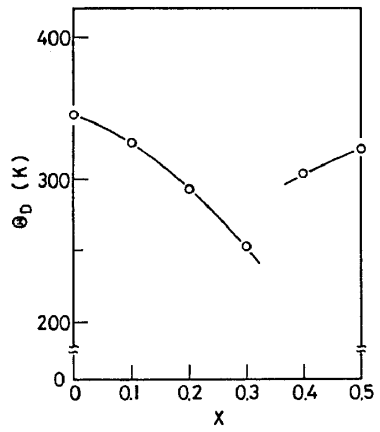

Fig. 5 Mn concentration dependence of $\Theta_D(0)$ for $(Co_{1-x}Mn_x)_{76}B_{24}$.

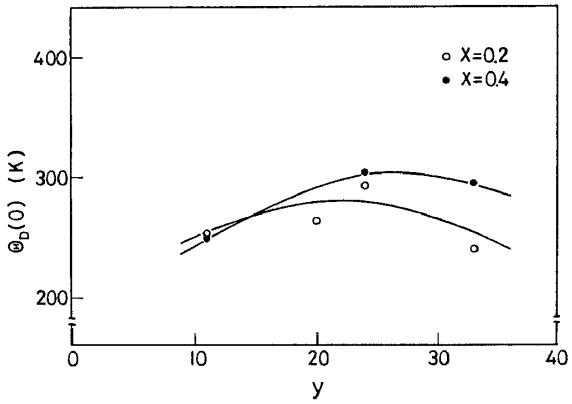

Fig. 6 B concentration dependence of $\Theta_D(0)$ for $(Co_{1-x}Mn_x)_{100-y}B_y$ for x=0.2 and 0.4.

due to Mn atoms does not explicitly appear in the magnetic states the frustration may occur locally in the surroundings of Mn atoms. This local frustration is not sufficient to cause the spin glass transition in a whole system at low temperature but must give a large magnetic contribution to the linear term in specific heat.

The Mn concentration dependence of $\Theta_D(0)$ of CMBX-24 series is exhibited in Fig. 5. $\Theta_D(0)$ is calculated from Eq.(3) for low temperature region ($T \lesssim 10K$). The very interesting result can be seen from this figure, that is, a deep minimum or a sharp discontinuity occurs in $\Theta_D(0)$ between x=0.3 and 0.4. This discontinuity in $\Theta_D(0)$ reflects a change in phonon behaviour which must arise from substantial differences in the amorphous microstructure. This discontinuity lies on a Co/Mn ratio close to that at which a martensitic transformation from hcp phase to fcc one occurs in crystalline Co-Mn alloys. Such kind of discontinuity or anomaly in the amorphous alloys at a certain concentration which corresponds to the phase boundary in the crystalline state also can be seen in the other physical quantities, for example, magnetic anisotropy for the (Fe-Co-Ni)-Si-B[14] amorphous series.

Figure 6 shows the B concentration dependence of $\Theta_D(0)$ for CMB20-Y and CMB40-Y series. As seen from this figure, it is evident that $\Theta_D(0)$ does not change so much with B concentration for both series. But it can be seen that $\Theta_D(0)$ has a broad maximum at about

20 ∿ 30% B concentration for both series. This may be caused by a maximum enhancement of the phonon term to $\Theta_D(0)$ due to the strongest chemical bonding at this concentration. The relatively low values of $\Theta_D(0)$ in amorphous alloys in comparison with crystalline alloys are generally due to a lack of any long range order causing a softening of transverse phonon modes which enhance C_L at low temperatures[16]. Mizutani has mentioned[16] that a characteristic feature of an amorphous alloy represented by a large δ coefficient in δT^5 term and a low $\Theta_D(0)$ is merely caused by a relatively low packing fraction of atoms. But in several amorphous alloys containing B atoms, the value of Θ_D is relatively large because of existence of coupling between B and metal atoms. Mizutani suggested that TM-B amorphous alloys have a large Θ_D compared with TM-P, Si or TM amorphous alloys because TM-B has a stronger bonding. A relatively large Θ_D in the present alloy series may be attributed to this covalent bond.

In the high temperature region ($T \gtrsim 10K$) the behavior of $\Theta_D(T)$ is rather complex because the low energy phonon excitation arises, and therefore $\Theta_D(T)$ deviates from the ideal Debye model. Moreover, in the spin-glass alloys, the magnetic specific heat is very large and usually its behavior would not be linear against temperature and becomes more complex in the high temperature region. Therefore in the present stage, it is very difficult to analyze the temperature dependence of $\Theta_D(T)$.

IV. Summary

$(Co_{1-x}Mn_x)_{100-y}B_y$ amorphous alloys were prepared by a melt quenching method from mother alloys. The low temperature specific heat as a function of Mn and B concentrations has been investigated in the temperature range between 0.4 and 50K. The main results are summarized as follows. i)The specific heat(C_p) in the present alloys can be well fitted to the ordinary expression $C_p = \gamma T + \beta T^3$ below about 10K. ii)The present alloys in the spin-glass region have large linear coefficient γ which must be attributed to the large magnetic contribution due to the frustration in the spin system. Even in the ferromagnetic region having high Mn concentration, γ values are rather large, since the Mn atoms may cause the frustration in the spin system, locally. iii)The low temperature limitation of the Debye temperature $\Theta_D(0)$ as a function of Mn content shows a sharp discontinuity between x=0.3 and 0.4. This discontinuity reflects a change in phonon behaviour which must arise from substantial differences in the amorphous microstructure.

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